

**GROUND-BASED AND AIRCRAFT MEASUREMENTS
OF TRACE GASES IN PHOENIX, ARIZONA (1998)**

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Abstract. In May and June of 1998, an extensive measurement campaign was fielded in the city of Phoenix and its environs. Measurements were made at ground sites and aboard the Department of Energy's G-1 research aircraft in an effort to understand the production of O₃ in this area. Diurnal variations in O₃ differed at the upwind Palo Verde, downtown Phoenix Super Site, and downwind Utery Pass surface stations. Air masses entering the metropolitan area had O₃ concentrations greater than 40 ppbv. Maximum O₃ concentrations near 100 ppbv were observed downtown at 14:00 local standard time; similar concentrations occurred much later in the day at the downwind site. One aircraft case study on June 5, 1998 is presented to illustrate ozone production in the region. Calculated ozone production rate and efficiency varied from 1 to 7 ppbv h⁻¹, and 1 to 3 molecules of O₃ per molecule of NO_x, respectively, for this flight. Hydrocarbon apportionment, based upon ground site and aircraft measurements, establish that biogenic hydrocarbons are not important contributors to O₃ production in the Phoenix area. Therefore, carbon monoxide becomes a major contributor to OH reactivity as the more reactive anthropogenic hydrocarbons become depleted. The relatively low ozone production observed in this study is attributed to a low rate of radical production in the dry atmosphere.

1. Introduction

The U.S. Department of Energy Atmospheric Chemistry Program (DOE/ACP) and the Arizona Department of Environmental Quality (ADEQ) conducted a field program to investigate tropospheric ozone formation in the Phoenix, Arizona metropolitan area May 15 - June 15, 1998. The motivation was to extend the findings of the many studies that have focused on understanding O₃ production in the northeastern and southeastern regions of the United States (Solomon et al., 2000 and references therein). We anticipated that ozone formation rates and efficiencies in the Phoenix area would differ significantly from those observed in the eastern United States for a number of reasons. The mix of pollutants in the region is dominated by on- and off-road vehicle emissions; industrial and other point sources contribute less than in the eastern and southeastern United States. Sparse vegetation cover in the southwest results in low emissions of biogenic hydrocarbons, which in other locations contribute significantly to ozone formation. In addition to these different emission profiles, complex terrain in the Phoenix urban area causes air flow reversals, and the contribution of these complex flows to multi-day episodes is unknown (Ellis et al., 1999). Finally, the low humidity, high solar intensity and large boundary layer height characteristic of the region create processing conditions that are markedly different than those in the Eastern U.S. This study explores the composite effect of these differences on ozone production in the southwest.

The Phoenix study included a linked set of aircraft and surface measurements designed to characterize the chemical and meteorological processes leading to ozone episodes. ADEQ's network of surface monitoring sites was augmented by additional sites and enhanced monitoring capabilities for the duration of the study. Wind profilers were deployed to characterize the atmospheric structure in the region. The DOE G-1 research aircraft, equipped with a comprehensive array of instruments to determine atmospheric trace gas and aerosol composition, flew over the region to evaluate the vertical and horizontal distribution of these species. Flight plans were designed to sample the boundary layer in three different domains: upwind, source region, and processed air downwind of the city.

This paper provides an overview of the field study, along with a summary of trace gas observations from the aircraft and diurnal trends at the surface. The vertical and geographical distribution of chemical species for aircraft flights are described and interpreted in the context of ozone formation. The reader is directed to related publications for additional details of the boundary layer meteorology (Fast et al., 2000; Doran et al., 2002), ozone production efficiency (Kleinman et al., 2002a) and photochemical age (Kleinman et al., 2003).

2. Experimental

2.1 Meteorological Conditions

Meteorological conditions during the Phoenix '98 field study have been summarized by Fast et al. (2000). The synoptic pattern was generally the same each day, with high altitude winds (> 2 km MSL) from the WSW all day. Drainage winds from mountains north and east of the city caused surface winds to veer from east to west on most days. High temperatures and low water vapor content resulted in mid-afternoon mixed layer heights reaching 2.5 - 3 km, significantly higher than the 1.0 - 1.6 km measured in Nashville in July, 1995 (Nunnermacker et al., 1998).

2.2 Surface Measurements

The Arizona Department of Environmental Quality (ADEQ, 1998) maintained a network of forty-two surface monitoring sites with different measurement capabilities during the study (Figure 1). Twenty five of these sites housed ozone monitors, and some included basic meteorological measurements, i.e., temperature, wind speed, wind direction, and relative humidity. Five special sites were outfitted with additional instrumentation to measure concentrations of O₃, CO, NO_y and SO₂. Additional highly instrumented supersites also included measurement capabilities for volatile organic compounds (VOCs) and carbonyls; these are identified in Table 1.

Measurements were made according to standard EPA protocol with commercial TEI analyzers (Thermo Environmental Instruments Inc., Franklin, MA). Data from the TEI analyzers were acquired continuously at all ground locations for twenty-four hours per day during the entire study (May 15 through June 12). Carbon monoxide was determined using a non-dispersive infrared gas filter correlation technique, ozone with UV absorption, and SO₂ with pulsed fluorescence. NO and NO_y were measured at surface sites using ozone chemiluminescence.

Modified VOC samplers (Model 910A, XonTech) with 6L stainless steel SUMMA type canisters were operated by ADEQ. Samples were cryogenically pre-concentrated in a freeze-out loop and then analyzed using high resolution capillary gas chromatography with flame ionization or electron capture detection. VOC samples were taken three times per day (07:00, 11:00, 15:00 LST) for a period of two hours.

Carbonyl compounds were measured at the supersites (see Table I) using C18 Sep Pak cartridges treated with dinitrophenylhydrazine (DNPH) and phosphoric acid. High-pressure liquid chromatography with UV detection was used to determine the carbonyl compounds. Cartridges were collected for a two hour period three times per day (as described for the VOC samples; except at Palo Verde (PV) - only once per day).

Hydrogen peroxide and total hydroperoxides were determined at Usery Pass (USY) using a continuous analyzer employing aqueous coil scrubbers for sample collection, followed by conversion to fluorescent products (Lee et al., 1990; 1994). Measurements were reported as hourly averages.

2.3 Aircraft Measurements

2.3.1 Instrumentation. The DOE Grumman G-1 aircraft was equipped with an array of instrumentation to measure trace gases and meteorological parameters. Both research-grade and commercial instruments were deployed; some of the latter were modified to enhance sensitivity and/or improve response time. Table II summarizes the measurement capabilities for the Phoenix study. Detailed information about the instruments can be found in earlier publications (Hubler et al., 1998; Williams et al., 1998; Nunnermacker et al., 1998). With the exception of peroxides and carbonyls, trace gas data were acquired with 1 s resolution; 10 s averages of the data were used for this analysis. The response time for peroxides was 1 minute (Weinstein-Lloyd et al., 1998). Continuous 3-minute average concentrations were reported for carbonyls (Lee et al., 1998).

2.3.2 Flight Descriptions. The four-week program consisted of 23 flights in 15 days, including eight days with both morning and afternoon flights (Table III). Morning flights, 2- 2½ hours in duration, were conducted between 08:00 and 12:00 LST. Figure 2a shows the typical morning flight pattern: an upwind leg, west of Phoenix, to measure background conditions, a triangular pattern over the city to characterize initial conditions and source emissions, and vertical profiles to 3 km both upwind and over the city. Afternoon flights retraced part of the morning leg over the downtown area, and probed a region further east to sample the processed urban plume. Afternoon flights, conducted between 14:30 and 18:00, also included a vertical profile approximately 40 km east of downtown (Figure 2b). The only exceptions were the May 27th morning flight, which included an extended upwind leg to sample background air, and the June 6th afternoon flight, which included an extended downwind leg.

3. Observations

3.1 Surface measurements

In this section, we discuss trends in trace gas measurements at Palo Verde (PV), selected to characterize air upwind of the city, downtown Phoenix Super Site (PXSS) and Central Phoenix (CP) sites, and Usery Pass (USY), a downwind site east of downtown (see Figure 1 for locations). Diurnal variations of ozone for the three regions between May 15 and June 13 are depicted in Figure 3. The highest ozone concentrations were observed during the afternoons of May 16th, May 24th and June 5th at all three sites. At PXSS, reaction with NO and deposition reduced ozone in the nocturnal boundary layer (NBL) below the detection limit during most nights. Complete loss of O₃ was evident fewer than half of the nights at PV, and never at USY, presumably due to lower NO_x emissions at these sites. Nighttime boundary layer dynamics at mountain sites also play a role (Aneja and Li, 1992). Differences between the three sites are more easily seen in composite diurnal profiles of O₃, CO, and NO_y (Figure 4). Features of these profiles are discussed below.

3.1.1 Upwind. Median ozone at PV showed a broad peak between 12:00 and 16:00 LST, with a maximum of 58 ppbv. The decrease in O₃ to a minimum of 20 ppbv at 06:00 LST coincides with an peak in NO_y reaching 11 ppbv. While southwesterly synoptic winds place PV upwind of the source region, surface winds were slow and had a S/SE component during the night and early morning hours. The anticorrelation of NO_y with O₃ suggests that O₃ was titrated by local NO_x emissions, and that the PV site is influenced by local sources during the night, perhaps the nearby highway. Concentrations of NO_y were at or below the detection limit of 0.4 ppbv during the rest of the day.

3.1.2 Downtown Phoenix. Diurnal variations downtown are illustrated in Figure 4 for the Central Phoenix (CP) site; other downtown locations exhibited similar patterns. Median ozone concentration peaked at 60 ppbv in the afternoon (15:00), similar to PV. Overnight, much higher NO_x emissions resulted in extensive titration of ozone

until 06:00. Values of NO_y as high as 400 ppbv and of CO as high as 5 ppmv were observed near midnight. The increase in O_3 concentration following breakup of the NBL can be attributed to a combination of photochemical production and downward transport of ozone from air aloft (see G1 observations below) (Shaw et al., 2002 and Berkowitz et al., 2002). Hourly average sulfur dioxide values, measured at four downtown locations, were always below 9 ppbv (detection limit = 1 ppbv). Since there are no significant sources of SO_2 in the region, SO_2 data were not analyzed further.

3.1.3 Downwind. On most afternoons, the USY site was downwind of the source region. A striking observation at this site was the relatively high concentration of ozone (median 50 ppbv) during the overnight period that represents regional background. Median ozone remained high during the early morning hours, and increased gradually in the afternoon to 60 ppbv at ~16:00. In contrast to PV and CP, the pattern of maximum concentration did not track that of median concentration at USY. For example, excursions in NO_y at 14:00 (top of the whiskers in Figure 4), were not reflected in the median. The maximum O_3 at this site also occurred several hours later than the median, and approximately 2 hours later than at CP. Although median ozone rose to 60 ppbv in the afternoon at all three sites, the maximum ozone at USY, which lies directly in the path of the urban plume under typical afternoon wind conditions, was on average 11 ppbv higher than at CP. These observations are consistent with transport of pollutants from downtown during the afternoon.

3.2 Hydrocarbon Abundance and Reactivity at the Surface

Hydrocarbon canisters were collected by ADEQ at upwind, downtown and downwind monitoring sites (PV, PXSS, and USY) allowing us to examine geographic and temporal differences in VOC abundance and OH reactivity. Average concentrations of anthropogenic and biogenic compounds at these sites for morning (07:00) and afternoon (15:00) sampling periods are given in Table IV. OH reactivity is calculated by summing the product of concentration (as ppbv) and OH rate constants for individual VOCs in each category. Propane is excluded because of the occurrence of very high concentrations in most of the PXSS afternoon samples. The biogenic category consists of isoprene, alpha-pinene, beta-pinene, and limonene.

Concentrations and reactivities are low except at the downtown site. For comparison a CO concentration of 200 ppb has an OH reactivity of about 1 s^{-1} . Biogenic compounds do not contribute a significant fraction of total carbon but because of their high reactivity account for 16 - 37% of total OH reactivity at PXSS and USY. These very reactive compounds make a lesser contribution to OH reactivity at mid-boundary layer altitude, as indicated in a following section where aircraft data is presented.

Anthropogenic concentrations and reactivities decrease from morning to afternoon due to diurnal variations in emissions and to the deepening of the boundary layer. However, changes are relatively small compared with the several-fold growth of the mixed layer between 07:00 and 15:00. Two measures of the intrinsic reactivity are given in Table IV. One is the ratio of anthropogenic OH reactivity to ppb carbon; the other is the ratio of ethylene to acetylene concentration. The latter ratio is of two compounds that are emitted almost exclusively in vehicle exhaust. Ethylene reacts with OH radical almost an order of magnitude faster than acetylene. Exposure of emissions to atmospheric photochemistry will therefore decrease the $[\text{C}_2\text{H}_4/\text{C}_2\text{H}_2]$ ratio. Table IV indicates that the afternoon samples are selectively depleted in ethylene. The afternoon ratio could be generated by exposing the air to an OH concentration of 5×10^6 for between 1 and 2 hours (Kleinman et al., 2003). According to the OH reactivity to ppbC ratio, which reflects a more diverse range of emission types, changes in intrinsic reactivity from morning to afternoon are small and can go in either direction.

3.3 Carbonyl and Hydroperoxide Measurements

Carbonyl measurements for three surface sites from May 18th through June 9th are shown in Table V. Formaldehyde, acetaldehyde and acetone are distinctly elevated downtown in comparison with upwind and downwind sites, while methyl ethyl ketone concentrations are similar upwind and downtown, but significantly lower downwind. Aircraft formaldehyde measurements also show high concentrations in the source region (Table VI). Average formaldehyde concentrations for surface sites and aircraft agree well except for downtown samples in the morning, when the average surface concentration was twice that seen on the G-1. However, the ratio of formaldehyde (HCHO) to VOC concentration is greater in the air than on the ground. In general, the downtown G-1 samples are more dilute than downtown surface samples, but have a greater proportion of oxidation products (Kleinman et al., 2003). Formaldehyde and NO_y concentrations were reasonably well correlated ($r^2 = 0.6$) during downtown G-1 transects, suggesting a vehicular source for formaldehyde (Altshuler, 1993).

Total hydroperoxide was measured at only one surface station, Usery Pass, between May 28th and June 9th. At this site, mixing ratios remained below 0.5 ppbv, and did not exhibit any discernable diurnal trend. On individual aircraft flights, median total hydroperoxide varied from 0.9 to 2.9 ppbv within the boundary layer. Average contributions to the total were 59% hydrogen peroxide, 33% from methylhydroperoxide (MHP), and 8%

from hydroxymethyl hydroperoxide (HMHP). For comparison, Nashville, TN exhibited higher concentrations of total hydroperoxide in the boundary layer (median = 5.2 ppbv) during the 1995 Southern Oxidant Study, with H₂O₂ representing 48% of the total and MHP 33%. HMHP represented 19% of the total, consistent with the greater abundance of its precursors, ozone and biogenic alkenes (Weinstein-Lloyd et al., 1998).

We present hydroperoxide measurements, segregated into upwind, source and downwind regions, in Figure 5. The four days depicted in the figure are the only days during the program for which hydrogen peroxide data for each of region is available for both morning and afternoon flights during a single day. On each morning flight, H₂O₂ was lower over the city than in background air. Afternoon H₂O₂ in the source region was lower than in the morning, and decreased still further downwind, consistent with inhibition of photochemical peroxide production in Phoenix and loss of H₂O₂ in incoming air masses as they traverse the source region. These conclusions are supported by photochemical calculations presented in a later section.

3.4 General Observations From Aircraft Studies

The relatively consistent meteorological conditions in Phoenix, coupled with repeated flight pattern around the metropolitan area, allowed us to characterize geographic patterns of trace gas abundances during the field program. We illustrate the influence of the source region by segregating flight data into four subsets: upwind and source region during morning flights, and source region and downwind during afternoon flights (see Figure 2). Summary statistics for the four subsets appear in Table VI, and general observations are described below.

Concentrations of CO, NO_x and NO_y in the source region and downwind were significantly elevated in comparison to upwind. We consistently observed elevated accumulation mode aerosols and NO_y as the aircraft crossed major roadways in the source region. Roadways parallel to the flight track often produced plumes extending tens of kilometers, broadened by surface level winds that shifted gradually during the day (see below). Median afternoon temperatures were only slightly higher than morning (21.9 vs 20.5°C), but water vapor concentration was more than 20% higher in the shallower morning boundary layer. Wind patterns changed significantly between morning and afternoon flights, with flows generally from the south to southeast in the early morning, becoming progressively more westerly during the afternoon. High wind speeds on most afternoons prevented the accumulation of photochemical products in the region. In the source region, peak afternoon concentrations of O₃ exceeded morning concentrations by approximately 10 ppbv, and were not substantially higher on the downwind legs.

4. Discussion

4.1 Comparison of Hydrocarbon Distribution for PXSS, Usery Pass, and the G-1

The distribution of hydrocarbon reactivity (i.e., the product $k_i[\text{VOC}]_i$) for 8 sampling days (May 26 - June 6) is illustrated in Figure 6. Source contribution was calculated based on hydrocarbon concentration and reactivity for aircraft data and the downtown (PXSS) and downwind (USY) surface sites where simultaneous measurements of CO and VOCs were available (Nunnermacker, et al., 1998). Aircraft data for the region over PXSS during morning flights and the downwind region near USY during afternoon flights were selected in order to compare aircraft to ground measurements, and to observe changes in apportionment with time. PXSS samples were taken at 07:00, before the mixed layer was fully formed, and showed the highest reactivity and largest fraction of anthropogenic VOCs. Pollutants from the source region undergo aging and dilution in the growing boundary layer during the average 2 hr transport time to USY, resulting in a threefold decrease in reactivity. The larger contribution of CO at USY reflects depletion of the more reactive hydrocarbons. Reactive hydrocarbons in downtown aircraft samples are depleted in comparison with surface samples. This is partially due to dilution, as they were taken somewhat later in the morning, and partially to reaction with OH. Hydrocarbon reactivity in downwind aircraft samples has declined further and, as in the ground site observations, CO has become the major contributor. The contribution of biogenic species to hydrocarbon reactivity is low in all samples, in contrast to observations in the southeastern U.S. For example, biogenic hydrocarbons contributed 25% of the reactivity in the urban plume during the 1995 Nashville study (Nunnermacker et al., 1998), in comparison to 4% in the Phoenix urban plume as determined from samples taken on the G-1. Thus, the contribution of biogenic hydrocarbons to O₃ production is not an important factor in the Phoenix metropolitan area.

4.2 CO/NO_y Relationship

CO and NO_x are co-emitted from vehicular sources that dominate the Phoenix emission inventory. CO and NO_y show a linear relationship for G-1 transects over the source region on morning flights. The average slope for six flights, 7.4 ± 1.0 ($r^2 \geq 0.70$), was somewhat lower than the value of 9 - 10 observed in earlier studies in automotive source regions (Parrish et al., 1991; Kleinman et al., 1998), but agrees with more recent values of 6.3 ± 0.9 made in Nashville, TN in 1999 by Parrish et al. (2002). These authors note that emission controls have resulted in a steady decline in CO to NO_x ratios, and that measurements show a rate of decrease faster than indicated by EPA emissions inventories. During the 2001 Phoenix experiment, data collected for downtown morning flights gave a CO vs NO_y

slope of 7.8 ± 0.9 , essentially the same as that obtained in 1998 (Berkowitz et al., 2002a&b). These values also are consistent with CO vs NO_y slopes of 6.3 ± 0.8 during early morning rush hours, measured at a downtown building during the Phoenix 2001 experiment (Spicer, private communication). CO vs NO_y slopes could not be determined for downtown surface sites in 1998 because data were provided only as hourly averages.

CO to NO_x emission ratios for Maricopa County for 1988 through 1999 are shown in Figure 7 (<http://www.epa.gov/air/data/index.html>). The regression line through the EPA data indicates a decreasing trend of approximately 3% yr⁻¹. Aircraft measurements for 1998 and 2001, and downtown surface data for 2001 fall along the EPA regression line and agree well with the decreasing emission ratio for CO to NO_y. Within experimental uncertainty, the CO/NO_y ratio from measurements is consistent with emission inventory data for Maricopa County.

4.3 Constrained Stationary State Calculations

Despite high concentrations of ozone precursors, afternoon ozone concentrations in Phoenix were only moderately higher in the afternoon than in the morning. We performed constrained stationary state (CSS) calculations (Kleinman, 2002b) to probe the factors that limit ozone production in this region in comparison to other urban areas. Calculations were based on RADM2 chemistry, augmented by Paulson and Seinfeld's isoprene oxidation mechanism and photolysis rates from Madronich's radiative transfer program. Concentrations of VOCs, CO, NO_x, O₃, HCHO, H₂O₂ and ROOH were constrained by aircraft observations. Calculations were performed for each time period during which a hydrocarbon canister sample was available. Hydrocarbon sampling locations (approximately 10 per flight) were chosen to represent different parts of the study region, and to capture events that appeared to be interesting based on real-time aircraft observations. We note that this sampling strategy yields a bias toward high-O₃ conditions. Trace gas concentrations were obtained by averaging data for the approximately 30s time periods that coincided with canister hydrocarbon sampling. The averaging time was extended for 1 minute in some cases to make up for missing or noisy data. These calculations yielded 108 data points for 20 flights. Results were segregated into subsets described earlier: upwind points early in the morning west of the city, the source region in the morning and in the afternoon, and downwind east of the city in the afternoon. Mean values of the calculated variables for these four areas are given in Table VII. The net instantaneous O₃ production rate (production minus loss) was only 3.7 ppb h⁻¹ during the morning flight over the source region, where concentrations of NO_x and reactive VOCs are highest. This is a consequence of the dry atmosphere, which results in a low value (0.6 ppb h⁻¹) for Q, the rate of radical production from the photolysis of O₃, followed by reaction of O(¹D) with H₂O. Approximately one third of the radicals arise from photolysis of HCHO in the source region and downwind.

Another consequence of the dry atmosphere is inefficient production of peroxides. If NO_x concentrations were zero, peroxide formation would be stoichiometrically limited to be half of the radical production rate (i.e. 0.3 ppbh⁻¹ at a Q of 0.6ppbh⁻¹). Calculated peroxide production (H₂O₂ + MHP) is ~0.1 ppbv h⁻¹ both upwind and downwind, but only at ~0.05 pptv h⁻¹ in the high-NO_x source region (Table VII). High NO_x concentrations effectively move radicals from peroxide- to NO_z-forming pathways. Slow chemical removal of NO_x by reactions with radicals, helps keep NO_x concentrations high. These processes, along with losses from dilution and deposition, explain the decrease in H₂O₂ concentrations illustrated in Figure 5. The CSS calculations suggest that low water vapor significantly limits photochemical ozone production in Phoenix, a conclusion that is explored further in the case study below.

4.4 Case Study - June 5th

One of the highest ozone days during the Phoenix program occurred on Friday, June 5th, when unusually weak winds furnished the potential for enhanced ozone production as precursor concentrations built up in the area.

The day began with high background ozone, illustrated by surface network measurements in Figure 8. Outside of the congested downtown area, where ozone was removed by reaction with NO, concentrations averaged 55 ppbv at 08:00. On the aircraft vertical profile between 800 and 2500 m, we observed a uniform O₃ concentration of 60 ppbv upwind at 09:50 and again over the source region at 11:30 (Figure 9). Ozone at the surface began to increase with the breakup of the nocturnal boundary layer, with most sites reaching ~60 ppbv by noon. In the source region, surface O₃ peaked at 77 ppbv at 15:00, while downwind sites peaked at higher concentrations early in the evening. For example, ozone at the USY site reached 86 ppbv at 18:50. Low wind speeds (0.5ms⁻¹) would result in a transport time of 4 to 10 hours between the source region and the nominally downwind site. Thus, we can attribute the increase in ozone in the source region and downwind ($\Delta O_3 \approx 17$ to 26 ppbv, respectively) to local production and transport during the afternoon.

The G-1 flight path over downtown Phoenix in the morning crossed numerous fresh pollutant plumes (i.e., NO_y > 10 ppbv and median NO_x/NO_y=0.61), shown in color in Figure 10. Based on location (over major highways), these plumes appear to be emissions from major traffic corridors. A correlation between PCASP and NO_x, was also observed in these plumes, as shown in Figure 11. By afternoon, plumes had grown to cover most of the source region, and the median ratio of NO_x to NO_y had decreased to 0.40 due to aging of the stagnant air mass

since the morning flight. The efficiency of ozone production (OPE), i.e, the number of oxidant molecules ($\text{O}_3 + \text{NO}_2$) formed per molecule of NO_x produced, is shown in Figure 12 for the source region in the afternoon. The slope of the regression line is 1.4 ($r^2 = 0.6$), consistent with values obtained in other high- NO_x regions where radical removal occurs primarily by reaction with NO_x (Daum et al., 2000a; Sillman, 2000). Figure 12 also shows that OPE for the downwind G-1 transect has increased to 3.7 ($r^2 = 0.84$). It is interesting to note that at this point the air has been processed ($\text{NO}_x / \text{NO}_y = 0.21$) and the system is under low- NO_x conditions. The trend toward higher OPE at low NO_x is a general feature of O_3 production in Phoenix (Kleinman et al., 2002a and elsewhere (Gillani et al., 2000; Ryerson et al., 2001). We note that the OPE obtained later in the day should be considered an upper limit because we have not corrected for loss of NO_y as the plume aged.

Results from CSS calculations for June 5th are given in Table VII. Instantaneous O_3 production rates in the source region varied between 1.3 and 6.7 ppb/hr, with a mean rate of 4.6 in the morning and 2.8 in the afternoon (Figure 13). The G-1 traversed the triangular path over the source region once at 10:33 - 11:26 and again from 16:05 - 16:36. During this 5.5 hour interval, average ozone increased from 62 to 83 ppbv. This observed O_3 increase of 3.8 ppb/h is within the range of the calculated rates. At the Usery Pass surface site, ozone concentrations were of the order of 58 ppbv at 07:00, characteristic of background air, as discussed earlier. By 18:30, ground O_3 concentrations had reached a maximum of 86 ppbv. The observed change in ozone concentration during this period is approximately 2.3 ppbv/h, in good agreement with the calculated afternoon value.

4.5 Comparison of Photochemistry in Downtown Phoenix vs. Nashville

Conditions on June 5th were similar to stagnation events in Nashville that generated ozone maximums during the 1995 Southern Oxidant Study (Valente et al., 1998; Daum et al., 2000a). We take advantage of this feature to compare details of ozone production between Phoenix and Nashville (Figure 14). The Phoenix metropolitan region had a range of ozone production rates from 3 to 6.7 ppb h⁻¹ and an ozone production efficiency between 1 and 3 for the urban plume. CSS calculations were performed for a G-1 flight in Nashville that occurred under approximately the same solar irradiance and ozone concentration. Data were further selected to have similar ratios of hydrocarbon to NO_x reactivity, $k_1[\text{HC}]/k_2[\text{NO}_2]$, ensuring that the hydrocarbon and NO_x mix was similar for the two regions. As a result, ozone production efficiencies, OPE_x , were ~ 2 ppb O_3 /ppb NO_x for both Phoenix and Nashville. The fifth set of bars, representing the fraction of radicals removed as nitric acid ($\sim 90\%$), confirms that the two cities were both in the hydrocarbon limited regime. Ozone production rate, $P(\text{O}_3)$, versus the quantity $Q\{k_1[\text{HC}]/k_2[\text{NO}_2]\}$ was linear, also indicating that ozone production was hydrocarbon limited (Daum et al., 2000b). $P(\text{O}_3)$ in Phoenix is approximately 5 ppb/hour, significantly lower than observed in Nashville. The significant difference is the rate of radical production, Q , which was twice as high in Nashville, a direct result of the higher water vapor mixing ratio. Further comparisons of ozone photochemistry in these cities can be found in the paper by Kleinman et al. (2002b).

5. Conclusions

- Ratios of CO to NO_y observed downtown and on the G-1 indicate that the trace gas mix in Phoenix is dominated by vehicle emissions. This ratio agrees with the decreasing trend in emissions published by EPA.
- Hydrocarbon distributions for both aircraft and ground sites established that biogenic compounds do not contribute greatly to ozone production in Phoenix. Anthropogenic hydrocarbons are the biggest contributor for both ground site and aircraft measurements with CO becoming more important as the plume ages.
- Ozone production in Phoenix is VOC limited based upon model calculations and is similar to one case observed in Nashville (1995). In general, Nashville had more days when ozone production was NO_x limited.
- The efficiency of ozone production in Phoenix (1998) was similar to that obtained in Nashville (1995). Ozone production rates were lower in large part because low humidity depresses the radical production rate.

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Table I. Intensive Sites for the Phoenix Study (1998)

Site	Measurements	Purpose
Palo Verde	VOC, NO _y , O ₃ , carbonyls, and surface meteorology	Background organic compounds
Downtown Super Site	VOC, NO _y , O ₃ , CO, carbonyls, and surface meteorology	Precursor concentrations in the source region
Usery Pass	VOC, NO _x , NO _y , O ₃ , CO, PAN, Peroxides, carbonyls, and surface meteorology	Downwind (i.e. processed air O ₃ precursors and oxidation products)

Table II. G-1 Instrumentation

Species Detected	Technique	Detection Limits	Time Response
NO / NO ₂ / NO _y	O ₃ chemiluminescence	<10 pptv, <50 pptv, <50	1 s, 4 s, 1 s
CO	NDIR gas filter correlation	~ 10 ppbv	1 min
O ₃	UV Absorption	2 ppbv	30 s
Aldehydes	HPLC/DNPH derivatization	10 - 20 pptv	3 min
H ₂ O ₂ , HMHP, MHP	PHOPAA/Fenton chemistry	60 pptv	1 min
hydrocarbons	Canister collection/GC analysis	10 - 100 pptv	post-flight analysis

Table III. Flight Summary

1998 Date	Flight Pattern¹	Start Time - End Time²
May 18	a	07:20 - 09:16
May 18	p	13:46 - 15:44
May 21	a	08:11 - 11:34
May 21	p	14:34 - 17:01
May 22	a	08:03 - 10:50
May 22	p	14:45 - 16:51
May 23	a	08:05 - 10:03
May 26	p	14:37 - 16:54
May 27	(3)	07:56 - 11:03
May 28	a	08:04 - 11:04
May 28	p	14:38 - 16:50
May 29	a	08:04 - 11:20
May 30	(4)	12:41 - 14:57
June 1	a	09:01 - 11:49
June 1	p	15:43 - 17:57
June 2	a	09:11 - 11:50
June 2	p	15:31 - 17:55
June 4	p	15:43 - 17:55
June 5	a	17:02 - 19:37
June 5	p	15:32 - 18:01
June 6	a	09:15 - 11:54
Jun 6	(5)	15:33 - 20:20
June 9	p	15:36 - 18:19

¹ Flight paths are typical morning (a) or afternoon (p) patterns (see text)

² Local time (= UTC - 7)

³ Regional flight, all upwind of city

⁴ Test flight

⁵ Regional flight, all downwind of city

Table IV. Average Hydrocarbon Concentration and OH-Reactivity

Site	Time of Day	Anthropogenic ^a				Biogenic ^b	
		Concentration (ppb C)	OH Reactivity (s ⁻¹)	k _{OH} / [ppbC]	[Ethylene]/ [Acetylene]	Concentration (ppb C)	OH Reactivity (s ⁻¹)
PV	a.m. ^c	18	0.71	0.038	0.87	0.20	0.063
	p.m. upwind)	13	0.57	0.42	0.64	0.10	0.025
PXSS	a.m.	198	10.4	0.052	0.82	5.5	2.0
	p.m. ^d	122	8.4	0.069	0.68	7.0	2.7
USY	a.m.	27	1.5	0.057	0.59	1.0	0.42
	p.m.	14	1.3	0.055	0.51	1.9	0.76

^aAll volatile organic compounds except aldehydes, biogenics and carbon monoxide.

^bBiogenics include: isoprene, alpha-pinene, beta-pinene, limonene. Methyl vinyl ketone and methacrolein were not included.

^cPV a.m. biogenic does not include one sample with a very high limonene concentration.

^dPXSS p.m. biogenic does not include 2 samples with very high limonene concentrations.

Table V. Average Concentrations (in ppbv) of Carbonyl Compounds at Phoenix Ground Sites

Site	Time of Day	Formaldehyde	Acetaldehyde	Acetone	Methylethyl ketone
PV	a.m.	1.21 ± 0.53	2.66 ± 0.3	4.03 ± 0.94	0.83 ± 0.07
PXSS	a.m.	3.44 ± 1.03	3.05 ± 0.6	7.02 ± 1.7	0.80 ± 0.20
	p.m.	2.01 ± 0.61	2.85 ± 0.47	6.59 ± 2.43	0.75 ± 0.42
USY	a.m.	0.74 ± 0.47	1.86 ± 0.49	3.90 ± 2.68	0.37 ± 0.33
	p.m.	0.78 ± 0.36	2.07 ± 0.29	3.11 ± 1.99	0.37 ± 0.24

Table VI. Summary Statistics for G-1 Flights

Species	Upwind (AM)		Source (AM)		Source (PM)		Downwind (PM)	
	Median	Max	Median	Max	Median	Max	Median	Max
O ₃ (ppbv)	51	84	54	101	62	95	65	96
NO _x (ppbv)	0.5	9.2	4.6	47	3.0	20	1.1	4.9
NO _y (ppbv)	3	13	11	61	7	30	5.4	16
NO _x / NO _y	0.24	0.69	0.49	0.80	0.41	0.55	0.17	0.27
CO (ppbv)	133	324	187	535	174	583	155	326
H ₂ O ₂ (ppbv)	1.1	2.8	0.8	2.6	0.8	1.4	0.7	1.2
MHP (ppbv)	0.7	1.7	0.7	2.3	0.5	2.5	1.0	2.3
HMHP (ppbv)	0.1	0.6	0.2	0.6	0.1	0.8	0.1	0.7
HCHO (ppbv)	1.10	2.22	1.76	3.74	1.66	3.54	1.41	2.11
PCASP (cm ⁻³)	233	808	333	1166	275	1224	222	1045
H ₂ O (g/kg)	4.45	7.54	4.38	7.58	3.60	6.10	3.38	5.24
Relative Humidity (%)	27	62	24	64	18	38	18	44
Temperature (°C)	20.8	25.4	22.4	26.7	23.3	31.6	21.0	31.1
Wind Direction (deg)	142	356	144	359	234	359	225	334
Wind Speed (m s ⁻¹)	2.3	7.4	3.0	11	4.1	10.8	5.5	14.1

Values above are calculated for all data points obtained at altitude < 2km

Table VII. CSS Calculations Mean Values

PARAMETER	REGION			
	upwind	source am	source pm	downwind
P _{peroxide} = peroxide production rate (ppb/h)	0.14	0.04	0.05	0.09
Net P _{peroxide} (ppb/h)	-0.06	-0.17	-0.20	-0.08
Q = radical production rate (ppb/h)	0.62	1.14	1.57	0.48
%HCHO = fraction of radical produced from HCHO photolysis	0.26	0.32	0.35	0.37
% O ₃ = fraction of radical produced from O ₃ photolysis	0.57	0.52	0.40	0.40
P _{O₃} = ozone production rate (ppb/h)	1.76	4.22	5.21	2.38
Net P _{O₃} (ppb/h)	1.35	3.68	4.71	2.01
L _N /Q = fraction of radicals removed as HNO ₃	0.44	0.85	0.87	0.48
n	9	49	26	24

all points are alt < 2km

FIGURE 1: Ground Site Locations

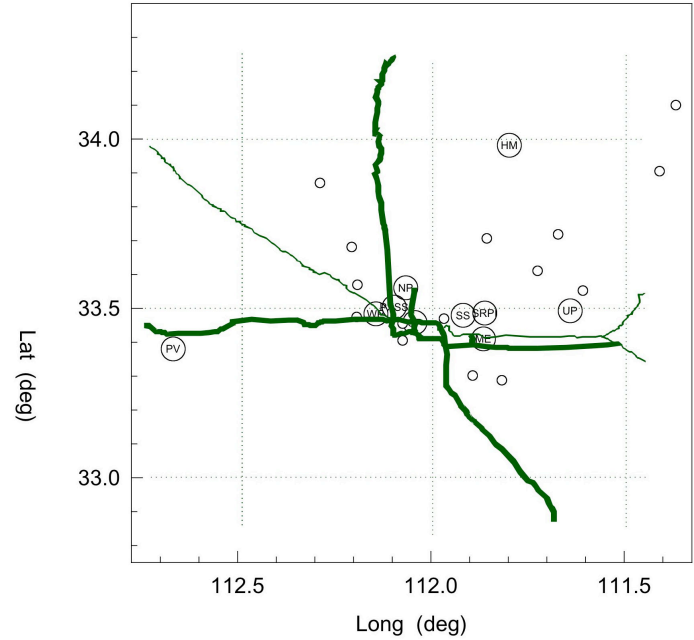


Figure 1. Sampling area, showing city limits, location of surface sites and major roadways.

FIGURE 2

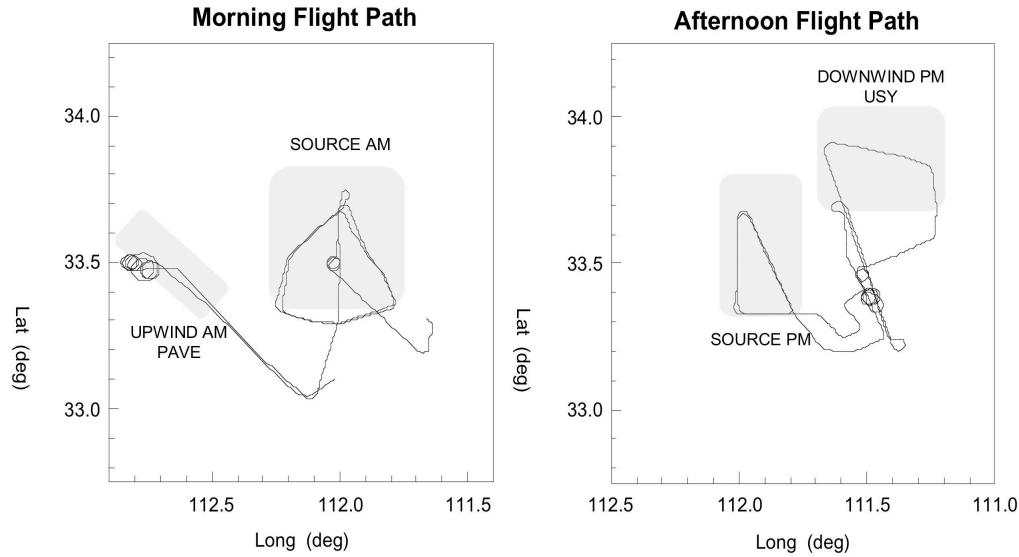


Figure 2. Typical morning flight pattern (a) and afternoon flight pattern (b).

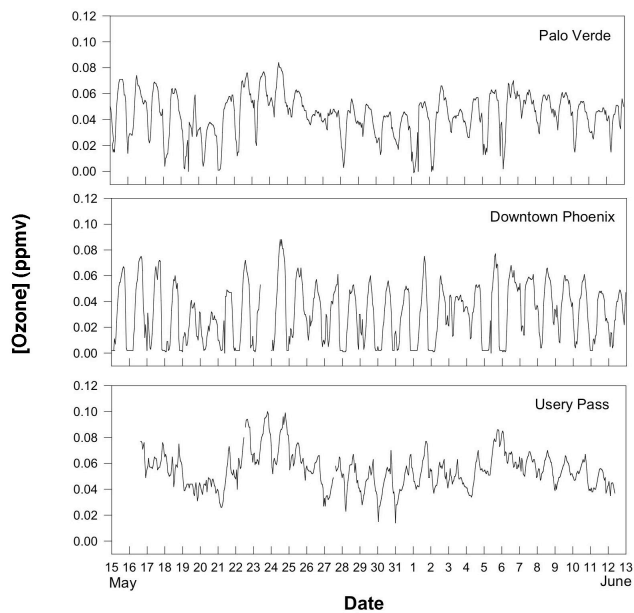


Figure 3.

Figure 3. Ozone time series for the entire sampling period at Palo Verde (PV), Phoenix Super Site (PXSS), and Usery Pass (USY).

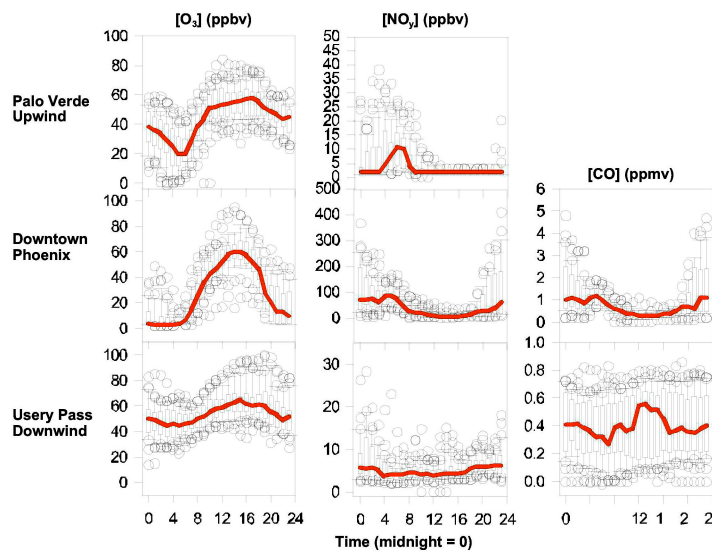


Figure 4.

Figure 4. Composite diurnal profiles of O₃ and NO_y at the Palo Verde (PV) surface sites. Composite diurnal profiles of O₃, CO, and NO_y at the Central Phoenix (CP) and User Pass (USY) surface sites. Rectangles enclose the central 50% of data and 10th and 90th percentile range is depicted by whiskers. Medians are shown by heavy lines and maximums are shown by a open circles.

FIGURE 5: Daily H_2O_2 trend

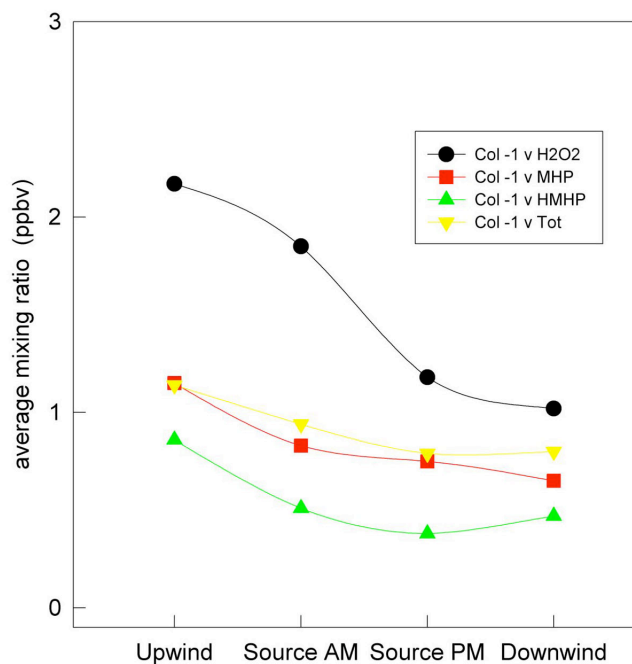


Figure 5. Daily average hydroperoxide trend for upwind, source, and downwind regions. All samples collected below 2 km. Data taken from four days containing both morning and afternoon flights.

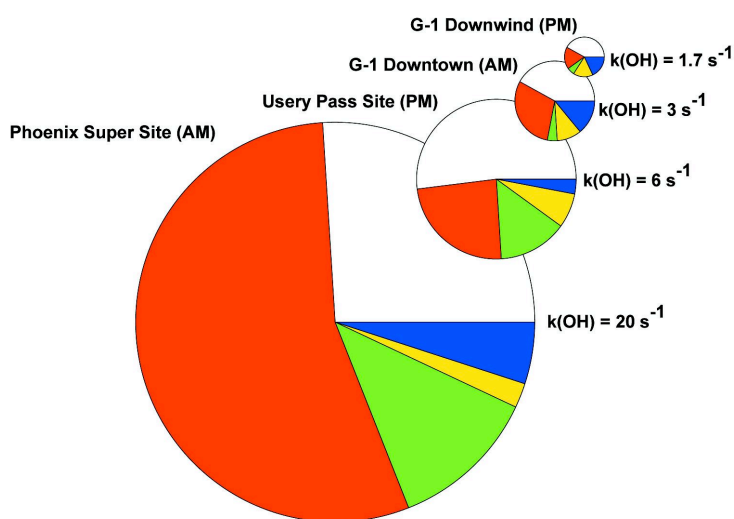


Figure 6.

Figure 6. Hydrocarbon distribution in Phoenix for specific categories: nonmethane hydrocarbons, carbon monoxide, isoprene, methane and formaldehyde. Data shown for PXSS and USY surface sites, and for aircraft samples obtained on flight legs DT and USY. Diameter of circle scaled to OH reactivity, i.e., $\sum k_i[\text{VOC}]$ for that location. NMHC = red; White = CO; Green = Isoprene; Yellow = CH_4 , Blue = HCHO.

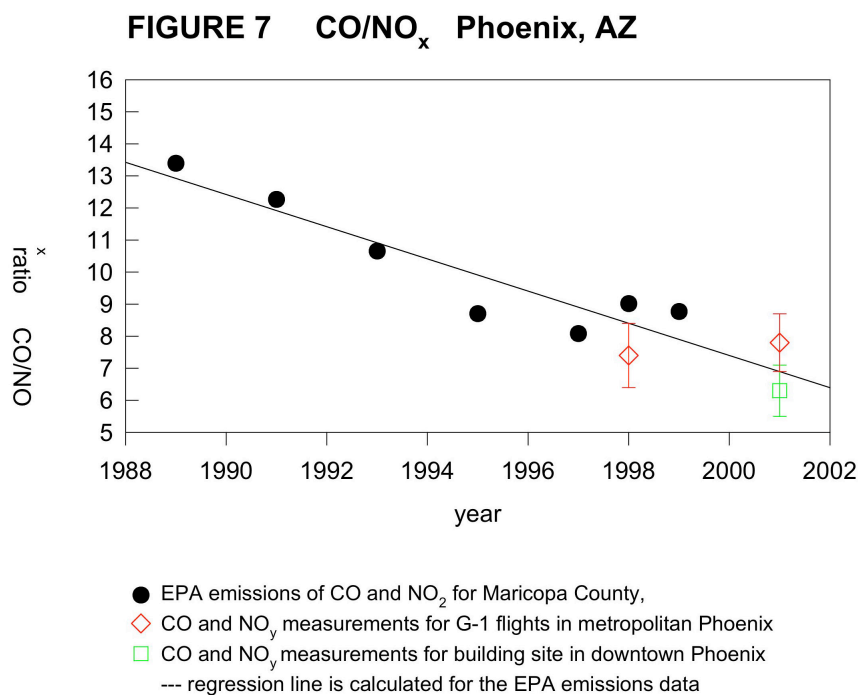


Figure 7. CO/NO_y from EPA emissions, G-1 flights (1998 and 2001) and downtown (2001).

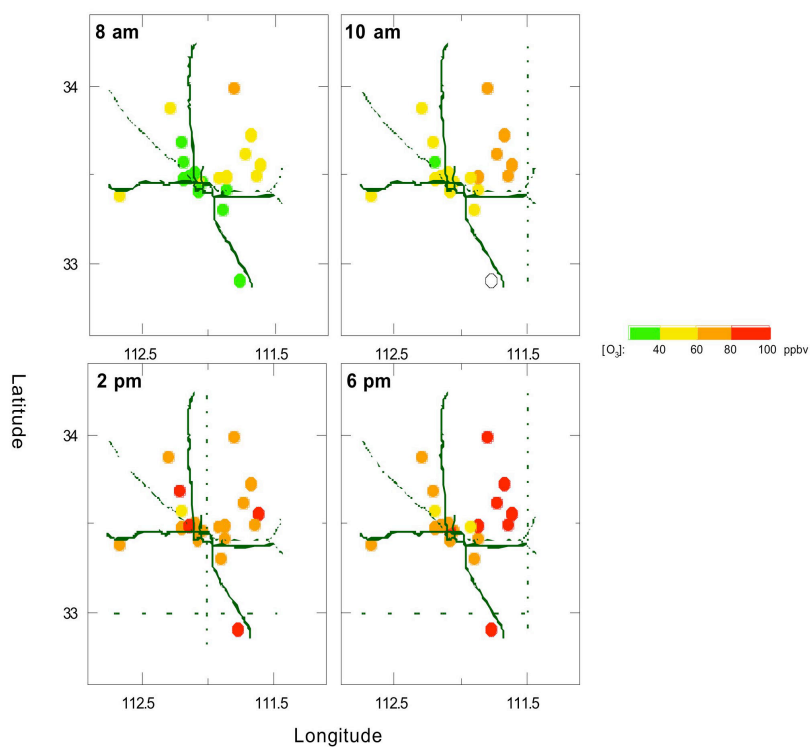


FIGURE 8: June 5, 1998 Phoenix Ground Sites

Figure 8. Ozone concentrations observed at ground sites on June 5, 1998.

FIGURE 9 OZONE VERTICAL PROFILES

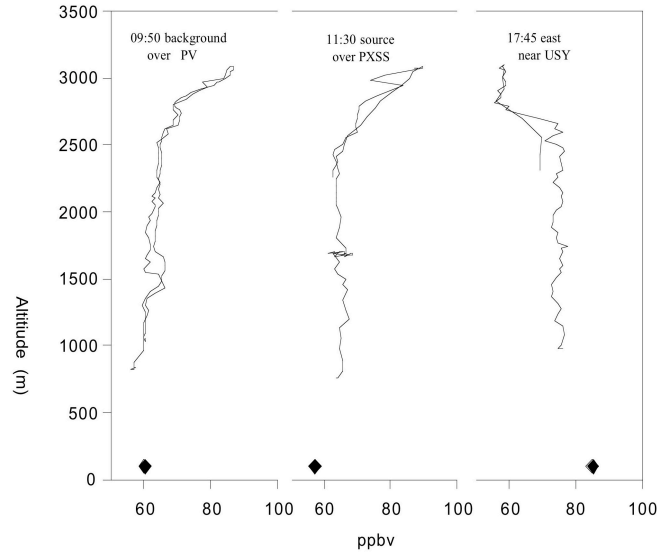


Figure 9. Vertical profiles of trace gases observed on June 5, 1998: At 09:50 a sounding was taken on the upwind flight leg near PV, at 11:30 a sounding was taken over PXSS and at 17:45 a sounding was taken near USY. Diamonds indicate ground site concentrations.

FIGURE 10

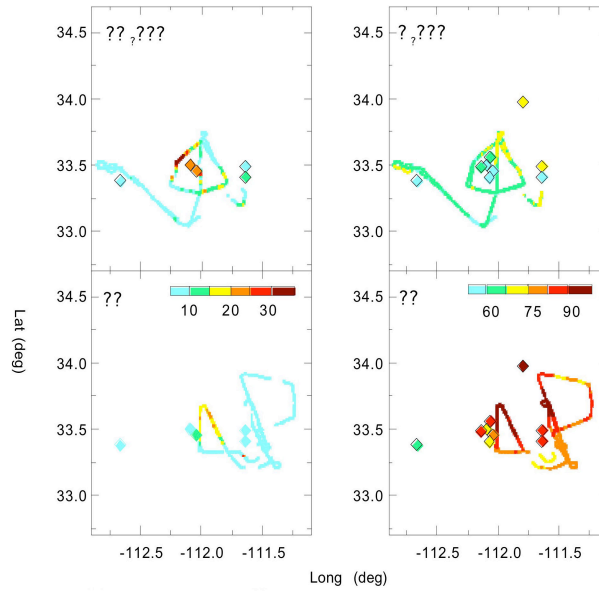


Figure 10. Flight path for morning and afternoon flights on June 5, 1998. Trace gas observations on specific flight legs discussed in the text. NO_y and O₃ concentrations along the flight track depicted in color. Ground based measurements indicated by diamonds.

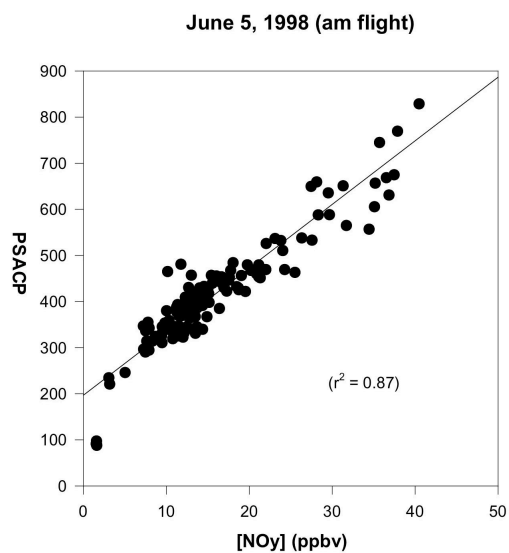


Figure 11.

Figure 11. Correlation of NO_y with PCASP during the afternoon flight on June 5, 1998. Only boundary layer data for this flight are included. The linear regression for NO_y vs. PCASP was $y = 197 + 13.8x$ ($r^2 = 0.87$).

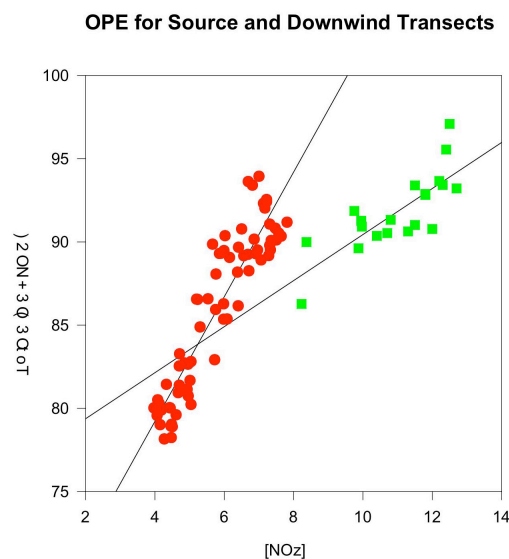


Figure 12.

Figure 12. Correlation of O₃ with NO_z during the afternoon flight on June 5, 1998. Only boundary layer data for this flight are included. The OPE_x for the downtown transect was 1.4 ($r^2 = 0.6$) (squares) and for the downwind (USY) transect was 3.7 ($r^2 = 0.8$) (circles).

FIGURE 13 CSS CALCULATIONS

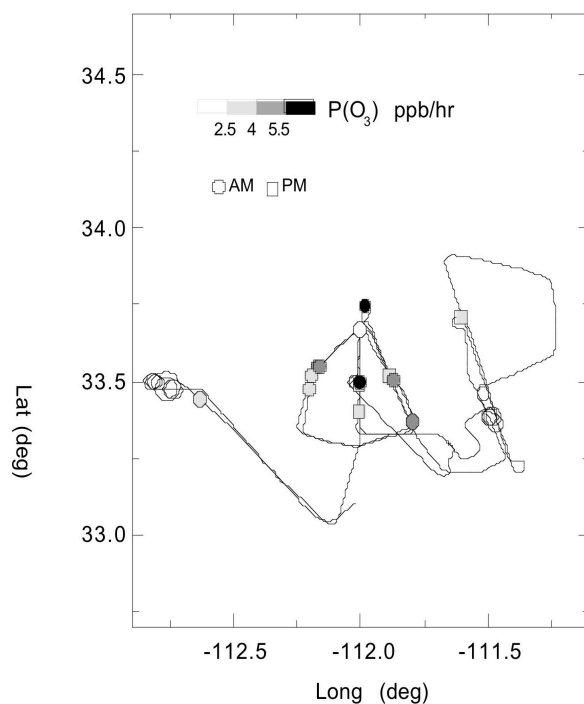


Figure 13. CSS calculated ozone production rates during the June 5, 1998 flight. Both morning and afternoon flights are included.

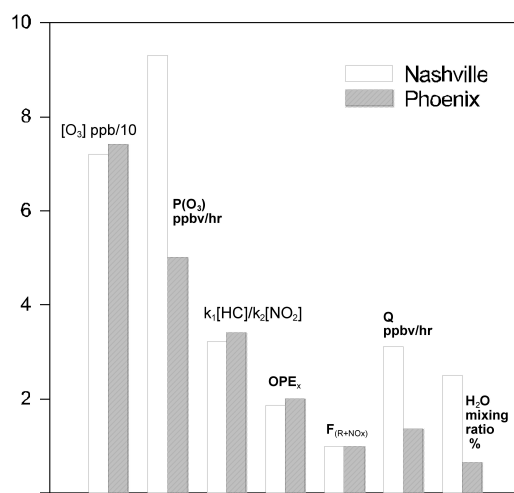


Figure 14.

Figure 14. Comparison of the CSS parameters for Nashville (1995) and Phoenix (1998).